Indian Journal of Pure & Applied Physics
Vol. 54, February 2016, pp. 144-148

Multiferroic properties of polyvinyledene fluoride/nickel nano-composites

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Received 3 November 2013; revised 6 March 2014; accepted 14 July 2015

Electrical and magnetic properties of ferroelectric polymer (polyvinyledene fluoride) and ferromagnetic metal [nanocrystalline nickel (*nc*-Ni)] composites have been investigated as a function of volume fractions of *nc*-Ni (f_{Ni}). A significant enhancement in saturation magnetization of 24 emu/g, measure of permeability (μ') of 1.11 and dielectric constant of 2050 at 100 Hz has been observed at the electrical percolation threshold (f_c) of the composite. The critical exponents (x and y) obtained are within the universal regime. The decrease of magnetization of the composite with decrease in f_{Ni} is attributed to the dilution effect and magnetic dipolar exchange interaction. The constancy of coercive field (H_c) has been explained on the basis of Stoner-Wohlfarth model. The value of μ' increases linearly with increase of f_{Ni} as the magnetic flux concentrates over individual n_c-Ni clusters/particles even beyond f_c. On the other hand, the value of μ' decreases for pure n_c-Ni probably due to the increased connectivity among the n_c-Ni clusters/particles and hence being a conductor results in eddy current generation in alternating magnetic field. The enhancement of dielectric constant near f_c is explained with the help of boundary layer capacitor effect.

Keywords: Composite materials, Percolation, Critical exponent, Permeability, Multiferroic

1 Introduction

The study of composite materials has been the subject of considerable interest in recent years because of their possible technological applications. The soft magnetic nano-composites or insulating polymer magnetic nano-composites (PMC) with nano sized metallic inclusions are common in established industrial applications because of the following properties/reasons. The composite of metal and insulator undergoes an insulator to metal transition (IMT) at a critical concentration of the metal, called electrical percolation threshold (f_c). This is characterized by the divergence in real part of dielectric constant and abnormal increase in its ac conductivity[1] at f_c. With increase of conductor fraction in the insulating polymer matrix, the effective dielectric constant (ε_{eff}) and effective ac conductivity (σ_{eff}) of the composites have been observed to approach to very large values[2-6] at f_c and interesting optical properties have also been found[7]. A similar type of behaviour is also observed in the variation of inductance[8] and imaginary part of permeability[9-11] for magnetic metal-insulator composite systems at f_c. In case of ferromagnetic metal nano particles, the nano-dimensional metal granule is considered as a ferromagnetic particle possessing an intrinsic magnetic moment equal to the sum of magnetic moments of the atoms contained in this granule. If the energy of the magneto-static interaction between granules is below k_BT (k_B is Boltzmann constant and T is the absolute temperature), no correlation between the magnetization vectors of such particles takes place, and the composite is expected to show its paramagnetic/super paramagnetic properties. When an infinite network of contacting granules is formed in the insulator matrix, at a critical concentration of the magnetic filler particle called magnetic percolation threshold[1,12-14] (m_c), conditions favouring exchange interaction between the atoms of the neighbouring granules in the matrix are expected[12-14]. Hence, the material should acquire a drastic change in its magnetic properties (such as; dc magnetic susceptibility/magnetization/coercivity, etc). The multiferroic behaviour, dielectric relaxation, ferroelectricity and ferromagnetism have also been investigated in a lot of nanosystems[15,16] and/or composite ceramics[17-19]. Additionally, the composite of ferroelectric polymer, such as; polyvinylidene fluoride

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(PVDF) and magneto-strictive components show recent interest in magneto-electric effect[20,21]. Recently, magneto-electric effect is also observed in a lot of simple systems of ferroelectric oxides and Ni composites[22] such as BaTiO3/Ni (Ref. 22), PZT/Ni (Refs 23,24), as Ni is the highest magneto-strictive[22] metal among all the ferromagnetic metals. In the present paper, with the aim of achieving multiferroic/magneto-electric properties in a PMC along with the study of m_c and f_c, a composite of PVDF/n_c-Ni has been investigated as a function of frequency of applied signal and volume fractions of n_c-Ni (f_{Ni}).

2 Experimental Details

The synthesis of PVDF/n_c-Ni composites and the measurement of their electrical properties can be found from earlier literature[2]. Structural investigation was done with the help of X- Ray diffractometer (Rigaku miniflex). The frequency dependence of initial permeability of the composites were measured with the help of turn coil method[25] by passing 20 mA ac current through the pick-up coil, using Agilent 4294A impedance analyzer with the help of 42941A probe at room temperature in the frequency range 10 kHz - 10 MHz. FM hysteresis loop measurements were done with the help of a homemade VSM.

3 Results and Discussion

3.1 Structural and Micro Structural Studies

With increase of f_{Ni} in the composites, the intensity of XRD peaks corresponding to *fcc*-Ni phase increases with a corresponding decrement in intensity of peaks for PVDF (Fig. 1). These changes confirm the formation of a two-phase composite. However, the observed broadening of Ni peaks in the composites is attributed to nano-crystallinity of Ni due to the reduction of it's particle size.

The presence of two different phases in the composites can be observed from the optical micrographs (Fig. 2). The extent of in-homogeneity of distribution of metallic fillers (brighter clusters) in the polymer matrix increases with increase of f_{Ni} and hence, the cluster size increases.

3.2 Dielectric and Magnetic Studies

The enhancement in ε_{eff} in the neighbourhood of f_c and the critical exponents (s and s') is explained on the basis of "boundary layer capacitor effect" [1-6] and "percolation theory" [1-6]. The universal fractional power laws as a function of frequency in the vicinity of f_c[26-28], given by

$$\sigma_{eff}\ (\omega, f_{Ni} \approx f_c) \propto f^{\,x} \qquad \dots (1)$$

and

$$\varepsilon_{eff}\ (\omega, f_{Ni} \approx f_c) \propto f^{\,y} \qquad \dots (2)$$

where f_{Ni} is the volume fraction of n_c-Ni, ω is the frequency of applied ac signal, x and y are the critical exponents, have been fitted to the experimental results of the composites (Fig. 3). The critical exponents obtained from the fit for $f_{Ni} \rightarrow f_c = 0.27$ (x=0.86 and y=0.16) are slightly above the universal values[26,27] (x=0.72, y=0.28). As predicted under the intercluster polarization model the relation[26,27] $x+y=1$, is well satisfied for $f_{Ni} \rightarrow f_c = 0.27$ while $x+y > 1$ for f_{Ni} (0.25) < f_c=0.27 (Fig. 3). The variation of σ_{eff} as a function of frequency at different f_{Ni} is shown in Fig. 4. It is

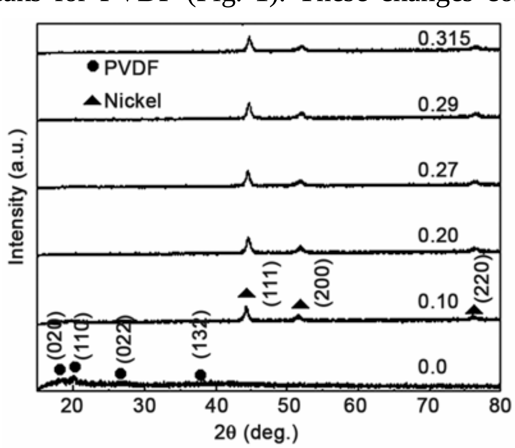

Fig. 1—X-ray diffraction pattern of PVDF/n_c-Ni composite samples for f_{Ni}=0.0 to 0.315 from bottom to top respectively

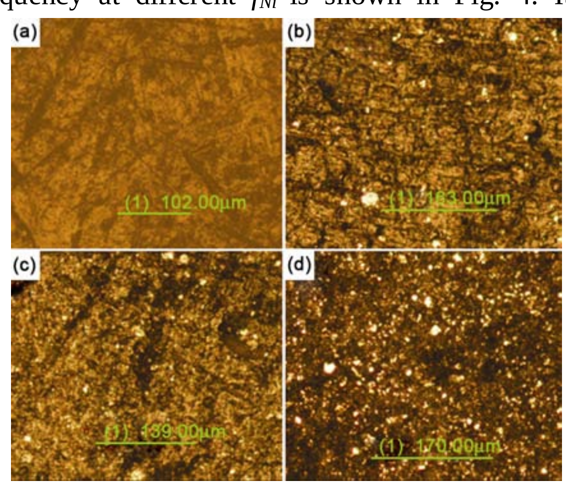

Fig. 2—Microstructure/optical micrographs of the polished surface of the pure PVDF and PVDF/*nc*-Ni composite samples (a) f_{Ni}=0.0, (b) f_{Ni} =0.10, (c) f_{Ni} =0.20 and (d) f_{Ni} =0.28, respectively

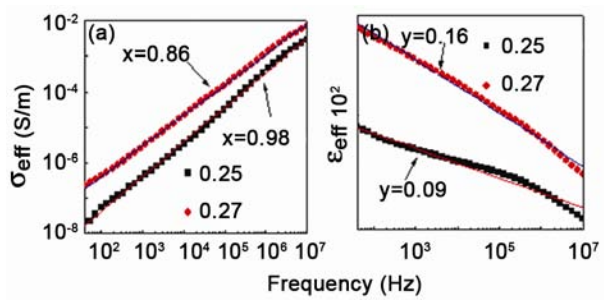

Fig. 3—Fitting of (a) Eq. (1) and (b) Eq. (2) to the results of two samples f_{Ni} =0.25 and 0.27 to obtain the critical exponents x and y respectively in the vicinity of f_c

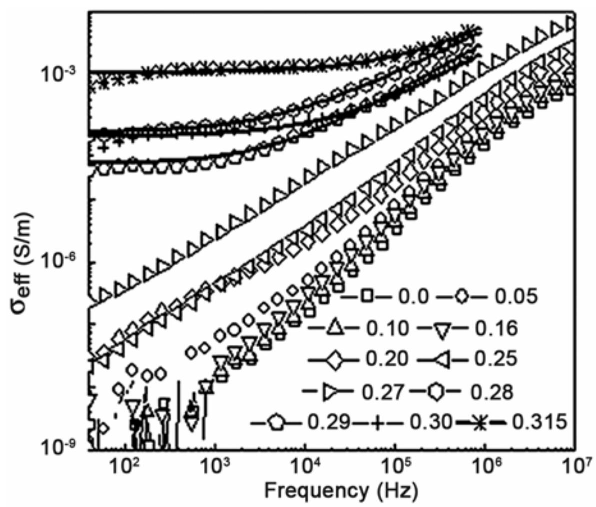

Fig. 4—Fitting of Eq. (3) to the experimental results of all samples under study to find the value of k

observed that the plot shows dispersion of ac conductivity with frequency for all the composites and the experimental results agree with the equation[29], i.e.,

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^{k} \qquad \dots (3)$$

with the values of k in the universal limit (0,1).

The ε_{eff} at 100 Hz and the saturation magnetization (M_s) of the composites as a function of f_{Ni} are shown in Fig. 5. The value of ε_{eff} rises from 255 to 2050 when f_{Ni} increases from 0.27 to 0.28. All the composites show typical ferromagnetic hysteresis (Fig. 6 and its inset) along with their magnetic saturation (inset, Fig. 5). The value of M_s increases from 7 emu/g for f_{Ni} =0.05 to 24 emu/g for f_{Ni} =0.28 with increase of f_{Ni} (Fig. 5). In order to extract the magnetic parameters, the room temperature *M-H* curves of all the composite samples are fitted to the usual function[30] customarily used to fit ferromagnetic hysteresis which is given by:

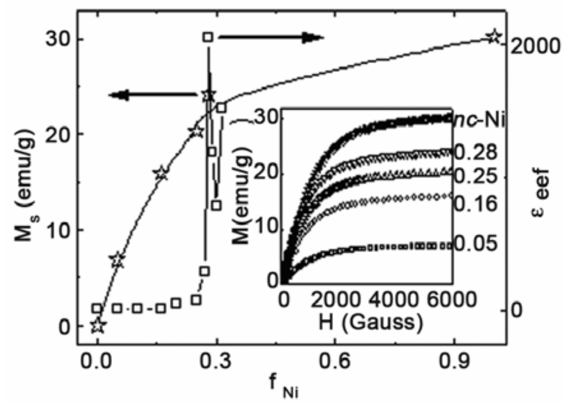

Fig. 5—M_s~f_{Ni} and ε_{eff}~ f_{Ni} for the composite samples with different f_{Ni} at 300 K [Inset: Initial magnetization ~Magnetic field plot for the composite samples (f_{Ni}=0.05 to 1.0) at 300 K]

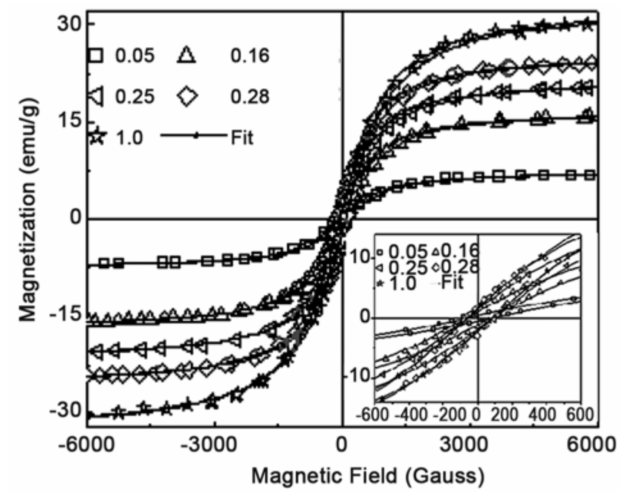

Fig. 6—*M~H* plots at 300 K for all the composite samples (f_{Ni}=0.05 to 0.28) and for pure n_c-Ni (f_{Ni}=1.0) [Inset: Expanded view of the plots showing hysteresis]

$$M(H) = \frac{2M_S}{\pi}\tan^{-1}\left[\frac{H \pm H_C}{H_C}\tan\left(\frac{\pi S}{2}\right)\right] \qquad \dots (4)$$

The quantities M_s and H_C give the saturation magnetization and coercivity of the samples, respectively where ‘S’ is known as “squareness” ratio of the ferromagnetic loop and is defined by the ratio of remnant magnetization (M_r) to saturation magnetization (M_s) of the ferromagnetic loop, i.e., $S=M_r/M_s$. Reasonably good fits of Eq. (4) to the magnetization curves have been obtained for all the composite samples (Fig. 6 and its inset). Table 1 compares the magnitude of M_s, M_r and H_C for all the samples obtained from the fits. As expected , it is observed from Table 1 that the values of M_s and M_r increase with increase of f_{Ni} while H_c remains constant

Table 1—Magnitude of the fitting parameters M_s, M_r, H_c, S for all the composite samples (f_{Ni}=0.0 to1.0)

f_{Ni}	M_s(emu/g)	M_r(emu/g)	H_c(Gauss)	Squareness ratio($S=M_r/M_s$)
0.0	0	0	0	0
0.05	7.6	0.46	74	0.06
0.16	17.0	1.14	72	0.07
0.25	21.8	1.66	74	0.08
0.28	25.8	1.95	73	0.08
1.0	33.2	1.9	74	0.06

(~72Oe) for all the composites. For single domain particles, the H_c value is expected to vary linearly with the packing fraction. However, the present paper does not show any change in H_c with packing fraction, suggesting the particles/clusters to be multi-domain. These results suggest that the non interaction of nickel with the polymer may be due to the complete phase separation of nickel from the polymer. It can also be understood that the value of H_c varies linearly with K_{eff}, where K_{eff} is the overall anisotropy constant per unit volume of the powder[17]. Since the value of K_{eff} mainly depends on the diameter of the well-crystallized Ni powders (Stoner–Wohlfarth model[32]), hence, K_{eff} can be approximately regarded as a constant (since diameter is constant) and that makes Hc as constant[17]. The rate of increment of M_s with f_{Ni} decreases with increase of f_{Ni} as can be observed from Fig. 5 that the slope (dM_s/df_{Ni}) of M_s~ f_{Ni} curve decreases with increase of f_{Ni}. This may be attributed to at lower f_{Ni} the particles/clusters are well separated from one another and the magnetic dipolar interaction between them is weak, which is also minimized because of the insulating, diamagnetic polymer matrix[31] forbidding the interaction between the particles. So the value of M_s decreases linearly with decrease of f_{Ni} in the region of $f_{Ni} << f_c$ that can be understood on the basis of dilution effect. As $f_{Ni} \rightarrow f_c$, the particles are very close to each other and the coupling between the magnetic moments of two or more clusters become prominent because of the increased dipolar interaction and that leads to lowering of rate of increment of M_s with f_{Ni} for $f_{Ni} \geq f_c$. The value of M_s for all the composites is achieved for the magnetic field, well above 3000 Oe (inset, Fig. 5).

3.3 Permeability Studies

Figure 7 shows the real part of permeability/initial zero field effective permeability (µ') as a function of f_{Ni} for various frequencies. The magnitude of µ' remains constant with variation of frequency up to 10 MHz (shown up to 1 MHz in Fig. 7). The magnitude

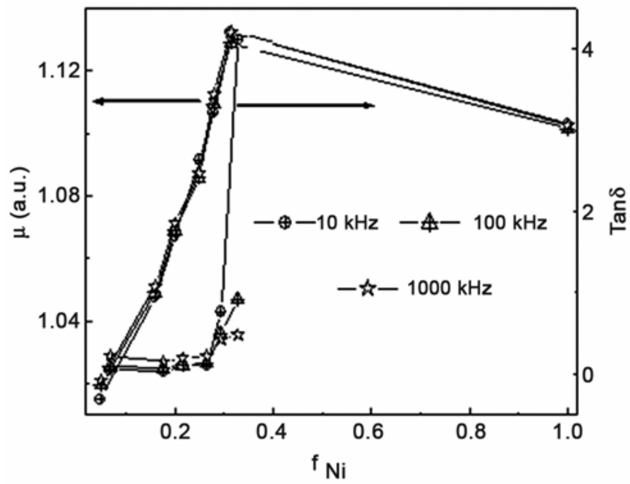

Fig. 7—Variation of zero field initial effective permeability and dielectric loss tangent of the composites as a function of f_{Ni} for different frequencies [Inset: AC conductivity versus frequency for the non-percolative and percolative composites]

of permeability is considered both due to the ferromagnetic properties of n_c-Ni and the generation of eddy currents by an alternating magnetic field[8-12]. The value of µ' of the composites for various f_{Ni} increases with increase of Ni content linearly even beyond f_c, i.e., up to f_{Ni} =0.315 and falls for pure n_c-Ni. Although the observed f_c value is f_{Ni} =0.28, the observation of magnetic anomaly beyond f_{Ni} =0.315 unlike that of earlier literature[8-12] may be attributed to the following. From literature[2], it is observed that the magnitude of loss tangent increases with increase of f_{Ni} (Fig. 7). The conductivity for the composite (f_{Ni} =0.25) is of pure ac conduction while the conductivity for (f_{Ni} =0.28 and 0.315) is of mixed type, i.e., the dc conduction in the lower frequency region followed by an ac conduction in the higher frequency region (Fig. 4). This type of mixed conductivity is the complete signature of a microstructure[2-5] in which, definitely the conducting particles are isolated from each other by a thin insulating polymer layer that prevents the generation of eddy current[11,12] in the samples. Hence, due to the non-setting of eddy current in the samples, the value of µ' increases linearly up to f_{Ni} =0.315 since the magnetic flux is more concentrated. But in the case of pure *nc*-Ni, the value of µ' decreases as compared to f_{Ni} =0.315 (Fig. 7) which may be due to the combined effect of ferromagnetic properties of *nc*-Ni and the generation of eddy currents by an alternating magnetic field.

Here the concept of m_c could not be realized in PVDF/*nc*-Ni composites which may be attributed to the presence of larger *nc*-Ni clusters in the polymer matrix giving rise to their individual permanent ferromagnetism arising due to their multi-domain nature. It is interesting to point out the ferroelectric behaviour of PVDF/*nc*-Ni composites has been explored[31], however, the magneto-electric effect, in such a simple system will be quite interesting and needs further investigation.

4 Conclusions

At f_c of PVDF/*nc*-Ni composites, a very high dielectric constant of 2050 at 100 Hz and a high M_s of 24 emu/g close to pure *nc*-Ni (30 emu/g) along with a higher value of μ'=1.11 is observed. The critical exponents found at f_c were in their universal region. The decrease of magnetization for the composites below f_c is explained with the help of dilution effect and magnetic dipolar exchange interaction. The increase of μ' linearly with f_{Ni} is explained on the basis of concentrated magnetic flux to the individual n_c-Ni clusters/particles and the non-generation of eddy current in the samples while its decrement is explained on the basis of generation of eddy current in the samples. The concept of m_c could not be realized due the presence of larger n_c-Ni clusters in the polymer matrix giving rise to their individual permanent ferromagnetism arising due to their multi-domain nature. The multi-functional properties of the composites may make them suitable for various applications, such as high charge storage capacitors, magnetic memories, high frequency applications, etc.

Acknowledgement

One of the authors (MP) gratefully acknowledges CSIR, New Delhi, India for providing the financial assistance to carry out this work at IIT, Kharagpur.

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